

## Special positions

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A recent PDB deposit from the CBB (returned with comments about errors) has prompted me to sensitize those of us who are less versed in crystallography about the significance of special positions and their consequence on refined parameters.

Special positions (in contrast to general positions) are occupied by atoms placed exactly at a point symmetry element. In macromolecular crystallography, there are only four point symmetry elements, all of course corresponding to pure rotations: 2, 3, 4, 6. By its operation, the symmetry element will generate additional copies of a point at a general (unrestricted) location  $x,y,z$ . However, if the original point resides on a point-symmetry element, its copy will coincide with itself.

Therefore, in structure refinement, an atom located at special position should have its occupancy factor divided by the order of the axis in question. In the case of a twofold axis and an atom that is part of a group with 100% occupancy, the atom's population should be set at  $1/2=0.5$ . This would mean that through the virtue of crystal symmetry it will be there 100% of the time anyway.

Special positions are easily recognized by the characteristic coordinates, corresponding to the location of a given symmetry element. In the International Tables for Crystallography vol. A (which you are strongly encouraged to consult, at least from time to time), special positions (if present) for each space group are listed with a notation introduced by Wyckoff; the Wyckoff positions specify the symmetry element responsible for a give special position and its (special) coordinates.

In the space group  $I222$ , there are many special positions, all located at the twofold axes of this space group. For example, a point with the coordinates  $0,0,z$  is located on the twofold axis along  $c$  (direction  $[001]$ ), passing through the origin. There is another twofold axis in this direction in this space group, passing through a unitcell face, and it generates special position at  $0,1/2,z$  (and at  $1/2,0,z$  through the Bravais lattice centering).

There are also special positions at intersections of point symmetry elements, and their multiplicity is increased (or atom occupancy - decreased) accordingly. In  $I222$ , three mutually perpendicular twofold axes intersect at  $0,0,0$  (unitcell origin). This position has point symmetry  $222$ ; an atom at  $0,0,0$  in this space group would have fractional occupancy of  $1/4$ .

Please note that in the space group  $I2_12_12_1$  there are also twofold axes (implicit!; they are *not* the axes listed in the space group symbol, which are screw axes and therefore cannot be sites of special positions!) in the three principal directions ( $[100]$ ,  $[010]$ ,  $[001]$ ). However, in this space group they do not intersect, and therefore there are no special positions with point symmetry higher than 2.

In macromolecular crystal structures, protein (or nucleic acid) atoms cannot normally reside at special positions because the macromolecules (individual polymer chains) do not possess this kind of symmetry. Quite often, however, water molecules can be found at axial positions, between macromolecules related by this particular axis. Other small-molecule components of the solvent can also reside at special positions. For example, a nitrate anion ( $\text{NO}_3^-$ ) could be

placed at a threefold axis with its plane normal to the axis direction. The N atom would have the occupancy of 1/3 then. The site symmetry could also be  $32$  (as in space groups such as  $P321$ ,  $P312$ ,  $R32$ ,  $P6_322$ , etc.) but would require the N-O bonds to be aligned with the twofold axes. Of course the  $\text{NO}_3^-$  ion could also reside on a twofold axis in the  $I222$  space group, with one of the N-O bonds along the axis. The special-position N and O atoms would then have occupancies of  $1/2$ , while the remaining two O atoms would have full (unchanged) occupancy.

Atom placement at special positions is mathematically equivalent to fixation (constraining) of some of the atomic parameters: (1) the coordinates themselves define the position and have to assume specified (exact) values, (2) the occupancy factor is reduced accordingly, (3) but also the ADPs (Atomic Displacement Parameters, formerly known as temperature factors) will be affected if they are represented by a second-rank tensor, i.e. are anisotropic. (Isotropic, i.e. scalar  $B_{\text{iso}}$  values, represented by a sphere, are not affected.) An anisotropic temperature factor is geometrically represented by a general (three-axis) ellipsoid (reflecting the amplitude of oscillation in different directions in space). If an anisotropic atom is located on a symmetry axis, then one of the ellipsoid's axes must be aligned with the symmetry axis and some of the cross (off-diagonal) terms ( $B_{ij}$ ) will have to be 0. If the axis order is higher than 2, then the ellipsoid will have to be axially symmetrical (two diagonal components,  $B_{ii}$ , equal), etc. The case of (symmetry-constrained) anisotropic ADPs is quite rare in macromolecular crystallography.

Clever crystallographic refinement programs (such as SHELXL) should be able to automatically detect atoms at special positions and fix their parameters, although specific complications can arise, e.g. deciding how "close to a rotation axis" is effectively equivalent to "on the axis", or reducing the occupancy of an atom in a group that as a whole already has fractional population.

If an error (mistake) with incorrect occupancy at a special position is detected at structure deposition stage, the solution of simply changing the occupancy, e.g. from 1.0 to 0.5, is not acceptable. The B factor of the involved atom would most likely change as well, which means that, unfortunately, the whole structure should be passed through another cycle of (hopefully correct!) refinement.

Further examples of special positions can be found in an educational paper about the use of vol. A of the International Tables for Crystallography [J. Appl. Cryst. 43, 1150 (2010)].

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08.03.2013